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## OBSERVATION OF SURFACE LAYERING IN A NONMETALLIC LIQUID

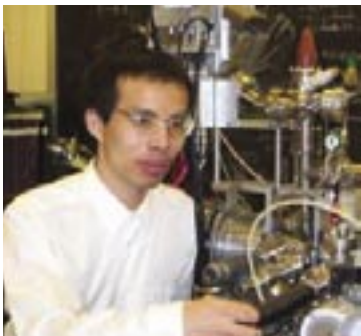
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*It has previously been reported, on the basis of synchrotron x-ray scattering studies, that many liquid metals have oscillatory density profiles (i.e. smectic-like layering) at their free surfaces. On the other hand, previous x-ray studies of many nonmetallic isotropic liquids have detected no such surface ordering. Is this effect due to the electron gas and therefore unique to liquid metals? We used x-ray reflectivity to study a molecular liquid, tetrakis(2-ethylhexoxy)silane. When cooled to 227K and below, the bulk remains liquid but density oscillations appear at the surface. There is only short-range lateral order, just as in liquid metals and unlike surface freezing. Our results confirm theoretical predictions that a surface-layered state will appear in any liquid at sufficiently low temperatures, if not preempted by freezing.*

The traditional picture of the free surface of a liquid is that the density changes monotonically from that of liquid bulk to that of the vapor. This picture describes dielectric liquid surfaces near room temperature quite well. However, x-ray scattering experiments have established that liquid metals and metallic alloy surfaces are layered.

Recently, Chacón *et al* concluded from simulations that surface layering will appear in any liquid below about  $0.2T_c$ , where  $T_c$  is the critical temperature, provided that it is not preempted by freezing. According to this theory, metallic liquid surfaces are found to be layered because they have high  $T_c$  values and so room temperature is below  $T/T_c \sim 0.2$ , while  $T_c$  is low for most dielectric liquids and so room temperature corresponds to  $T/T_c \sim 0.4 - 0.5$ . Many dielectric liquids will freeze above  $T/T_c \sim 0.2$ , making the necessary temperatures inaccessible. If one finds a dielectric liquid with relative high  $T_c$  and low melting point  $T_m$ , so that  $T_m/T_c$  is less than 0.2, one should be able to observe surface layering in this dielectric liquid.



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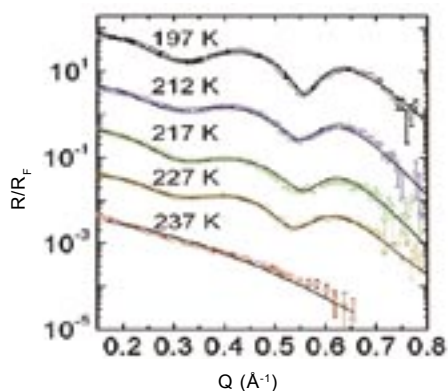
We have studied the surface of a molecular liquid, tetrakis(2-ethoxyhexoxy)silane (TEHOS), using x-ray reflectivity and confirmed the prediction of Chacón. TEHOS is an isotropic (non-

liquid-crystalline) dielectric liquid. The molecule consists of one Si and four O atoms in the center, surrounded by four saturated branched alkanes, forming a "wax coating" that makes the molecules nonreactive and roughly spherical. Viscosity measurements have shown that it is a fluid down to at least 219 K. Using x-ray scattering in transmission, and differential scanning calorimetry, we have found no evidence of a bulk phase transition down to 190 K. Its  $T_c$  is estimated to be  $\sim 950$  K.

In order to easily cool the liquid, we prepared  $\sim 5000\text{\AA}$  films of TEHOS supported on silicon substrates, which were formed by putting a few drops of liquid on the substrates, allowing the liquid to spread, and then draining the excess. There is no interference between the two interfaces of the films because the film thickness is much larger than the x-ray coherence length. To avoid seeing features in the reflectivity due to solid-liquid interface layering, we prepared and used substrates with RMS surface roughness  $> 20\text{\AA}$ . We have confirmed that the scattering features due to interfacial layers can no longer be seen when the substrate surface is rough.

**Figure 1** shows the specular reflectivity  $R$  divided by the Fresnel reflectivity  $R_F$  at several temperatures. At 237 K (and at higher temperatures, not shown here), the scans are featureless, similar, to those from typical nonlayered dielectric liquid surfaces. At lower temperatures, distinct reflectivity oscillations are seen. A peak occurs at about  $0.6\text{ \AA}^{-1}$ , which matches precisely the peak position of the bulk scattering data, and signifies that the layering occurs at the surface. The temperature threshold corresponds to  $T/T_c \approx 0.25$ .

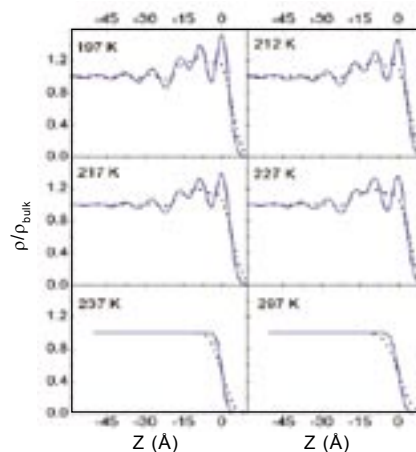
We fit the data in **Figure 1** by modifying the ‘semi-infinite series of Gaussians’ model frequently used to fit reflectivity data from liquid metal surfaces. Good fits were obtained as shown as solid curves in **Figure 1**. **Figure 2** shows the electron densities obtained from the fit. The dashed lines are the best-fit density functions; the solid lines are the same functions with the capillary width set to zero. In other words, the solid lines show what the surface profiles would look like if they had not been broadened by thermal capillary waves. The profiles show that at high temperature the density



**Figure 1.** Normalized specular reflectivity for ~5000 Å TEHOS films on rough silicon wafers at different temperatures. Lines are best fits using the electron density profiles shown in Figure 2. The data are displaced vertically for clarity.

changes monotonically, but at low temperatures there are layers. The in-plane scattering data show only liquid-like order, just as at liquid metal surfaces.

Our results confirm the theoretical prediction that dielectric liquids will show layered structure at the surface if cooled down to sufficiently low temperature. In other words, the surface-layered state is a general property of the liquid phase, not one that is limited to liquid metals.



**Figure 2.** The dashed lines show best-fit electron densities as functions of distance from the surface for ~5000 Å TEHOS films at different temperatures. The solid lines show the density profiles with capillary broadening removed.